

The mechanism of generating nanoporous Au by de-alloying amorphous alloys

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Abstract

De-alloying, i.e. selective dissolution of alloys, is currently studied to produce nanoporous gold items suited for use in catalysis, electrochemical applications, sensors and actuators. Both crystalline and amorphous alloys can be selectively etched. In the former, less noble atoms are removed from surface terraces of grains layer by layer, while noble ones form mounds. These evolve by undercutting and electrolyte percolation to form a ligament network. The mechanism of ligament development by de-alloying amorphous alloys is unknown. Here we show that for de-alloying a Au-based glass, in this case $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$, percolation of the electrolyte through cracks of the native surface oxide initiates the formation of protuberances which are soon undercut. An interlayer develops, where Au crystals germinate, grow to nanometer size by diffusion and impinge. This is how ligaments start to coarsen. The interlayer is found at all stages between coarsened ligaments and amorphous phase. The ligaments are defective polycrystals, as opposed to single crystals obtained from crystalline alloys.

Introduction

The selective electrochemical/chemical dissolution of less noble components of an alloy constitutes the process known as de-alloying [1]. The atoms of the remaining noble element diffuse along the solid-electrolyte interface forming clusters which progressively extend in three dimensions. A material is obtained made of continuous ligaments and open pores both in the nanometer range [2]. Large part of the information available to date on the electrochemistry of the process, as well as the resulting structure and morphology of ligaments, derives from experiments performed using two-component solid solutions, e.g. Ag-Au [3,4]. These are polycrystalline alloys having large grains, whose structure and size is retained after selective etching. Therefore, each grain becomes a porous single crystal [5]. Similar microstructures stem from a combination of dissolution and diffusion of de-alloyed multicomponent crystalline alloys (e.g. Ag-Au-Pt, Au-Cu-Mn-Zn), or intermetallic compounds having compact crystalline structure (e.g. Al_2Au) [6-8].

The events occurring during the electrochemical de-alloying of crystalline alloys are described according to the porosity evolution model [9-11]. Assuming a flat surface of grains, the stripping of atoms occurs layer by layer leaving the more noble Au on the surface, initially as adatoms. These are very mobile and agglomerate rapidly into clusters, while further layers are similarly etched. Consequently hillocks are formed, which passivate the alloy locally, trapping some less noble atoms. The distance between the hillocks is in the order of a characteristic diffusion length. The electrolyte percolates around the mounds inducing further de-alloying and undercutting them. The distance between a hillock and a neighbouring one increases and germination of new clusters [] occurs when it becomes approximately twice the characteristic diffusion length. The repetition of this process results in a continuous network of interconnected ligaments and pores [9-11].

Coarsening of this microstructure occurs on both prolonged etching and annealing. It has been earlier attributed to surface smoothening by diffusion. In later studies, ligament pinch-off due to Rayleigh instability in the solid state has been assumed [12]. Such atomic displacements should equally be controlled by surface diffusion. Actually, a number of kinetic studies have shown that coarsening is a thermally activated process with activation energy of the same order as that found in experiments on de-roughening of gold electrodes due to surface diffusion [13]. At variance, in a series of simulations the coarsening of the interconnected network was attributed to the mechanical collapse of neighbouring ligaments onto each other. After pinch-off at necks this should be driven by the reduction in energy when surfaces relax to their lowest-energy orientations providing compensation to the plastic work required to bend the ligaments [14]. Direct observation of these events is however lacking.

During the last few years, the de-alloying process was applied to alloys having complex structure, i.e. intermetallic compounds (e. g. Al_2Cu), quasicrystalline phases and multicomponent amorphous alloys [15-20]. Here, the removal of the less noble elements and the following surface diffusion of adatoms, induce the formation of numerous new crystals of a compact phase, rich in the noble components of the alloy, which are a few nanometers in size. In all cases, the original periodic or amorphous structure of phases is not retained being less stable than the new fcc phase. The crystalline domains grow as a function of time until they impinge onto other domains forming ligaments composed of several crystals, contrary to the case of de-alloying crystalline alloys [5]. Therefore, the morphology and microstructure of ligaments depends on the nature of the matrix from which they derive. It is, however, found that coarsening occurs in amorphous materials as well, in which case length scales of ligaments and porosity are of the same order as that found in formerly compact crystalline alloys [5]. Therefore, the question to be answered is how the mechanism of de-alloying complex structure alloys works in the early stages, as well as how the subsequent coarsening occurs.

To progress on this ground, we employ the $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ amorphous alloy, whose de-alloying kinetics on a long time scale is known [18-20], in order to study the electrochemical de-alloying process, up to the full development of ligaments and pores, using a combination of microscopy techniques.

Experimental Part

A $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ master alloy was made by arc melting the pure elements (Au, Ag, Cu, Pd, Si: all 99.99%) in Ar atmosphere. Ribbons were produced by melt spinning: the molten alloy was ejected through the nozzle of a silica crucible onto a Cu wheel rotating at 20m/s in a chamber evacuated and filled with an Ar partial pressure [18]. The ribbons are about 30 μm in thickness and 2 mm wide. Samples 15 mm in length were cut for use as anode in a PGSTAT302NPotentiostat/Galvanostat of MetroOhm Instruments in a three electrode cell. 1 M HNO_3 aqueous solution was employed for de-alloying at 70°C at the potential of 1.05V vs Ag/AgCl using a Pt grid cylinder as a counter electrode. These conditions were previously shown to yield de-alloying with success, producing a continuous and homogeneous nanoporous network [18-20]. A new sample was used as working electrode for every de-alloying experiment. Samples were de-alloyed for 30 s, 1, 3, 5, 10, 15 and 60 minutes.

A Bruker-Atomic Force Microscopy (AFM) Dimension Icon was used to examine the sample topography in tapping mode with a scanning rate of 75Hz. A Si tip on a nitride cantilever (ScanAsyst-Air) was used with a resonance frequency of 78kHz. The AFM data analysis is made by means of the WSxM5.0 Develop 7.0 software [21]. A Inspect FTM FEG Scanning Electron Microscope (SEM) was also used for checking the morphology of the samples that have been de-alloyed for 30 sec and 1 min. In both cases the samples were cut under tension load. The X-rays Photoelectron spectroscopy (XPS) investigations were performed with a PHI 5600 XPS system using monochromatic Al K α X-rays (350 W). For the depth profile, Ar⁺ ions were used with an energy of 3.5 keV and an angle of around 30 degrees to the surface normal. The sputtering rate is 0.7 nm/min measured with SiO₂ reference and the pressure in the XPS analysis chamber is 1*10⁻⁸Pa. Data analysis is made by means of PHI-MULTIPAC software [22]. A JEOL JEM3010 High-Resolution Transmission Electron Microscope (TEM) was used for the study of the ligaments of the de-alloyed samples after mechanical thinning, and a Scanning Tunneling Microscope (STM) was used for the characterization of the ligaments and the porous scaffold.

Results and discussion.

The surface topography of the as-spun ribbon which resulted amorphous in X-ray patterns shows a grain-like structure as revealed by AFM (Fig. 1a). The zones displaying uniform contrast are separated by fine cracks having depth of the order of 1 nm. The XPS depth profile of the ribbon is shown in Fig. 1b showing an excess amount of Silicon and Oxygen during the first 6 minutes of sputtering which correspond to a depth of about 4 nm. After this time, the values of the elemental concentration are stabilized at the level expected from the composition of the alloy. The Si:O ratio suggests the presence of a layer of SiO₂ on the surface. Therefore, the cracks refer to this layer apparently formed during the rapid solidification process. It is also noticed that there is a small enrichment of Au on the sub-surface layers of the ribbon. This does not hamper the etching of the alloy.

After de-alloying for 30 s new features appear on the surface in the form of self-similar hilly protuberances (Fig. 2 a and b) which reach a height of about 50 nm with respect to the background level. Their lateral extension is in between 100 and 200 nm [21]. It is inferred

the electrolyte starts penetrating into the alloy through the fine cracks of the oxide layer initiating the progressive etching at the length scale of these defects. This must differ from the initial stage of de-alloying binary Au-Ag and Au-Cu crystalline alloys not containing Si, where, however, it is likely that crystal defects such as dislocations, twins and grain boundaries emerge on the surface providing preferential sites for etching.

The fine structure of a sample de-alloyed for 30 sec, was analyzed by TEM as shown in Fig. 3. The sample was mechanically grinded to obtain a wedge before de-alloying. The image reports the microstructure of the zone of the wedge which was transparent to electrons. The dark zones contain mostly crystals with size of a few nanometers, randomly oriented. Their structure is fcc (diffraction pattern given in the inset of Fig. 3a). Rings in the pattern and lattice fringes are compatible with the lattice constant of Au. The mottled contrast of the zones in between them is due to a mixture of amorphous and crystalline phases. The latter being again composed of a large number of Au crystals. The overall microstructure appears to reproduce that displayed in the images of Fig. 2a. The Au enriched layer underneath the Si oxide was not thick or concentrated enough to cause passivation. Actually, here there might be some metal clustering in crystalline form since some Si is lost because of oxidation. These could constitute embryos for the first crystals which originate from de-alloying.

Once the process continues in the bulk, crystals are continuously formed with random orientation. This might suggest that they are progressively nucleated at the interface with the amorphous matrix contrary to the case of crystalline alloys in which the original grains do not change structure and provide a substrate for the epitaxial growth of ligaments. However, the process does not appear as a classical nucleation series of events since it is not reversible, i. e. embryos cannot dissolve back in the amorphous phase once less noble atoms are lost as ions into the electrolyte. The crystallization appears to be better described as spontaneous germination [23] occurring when Au atoms, freed of nearest neighbours, move to a short distance to self-assemble in their stable close packed structure. The size of the crystalline features observed by TEM after de-alloying for 30 s is compatible with a surface diffusion coefficient in the order of $10^{-19} \text{ m}^2\text{s}^{-1}$, which was determined for the surface movement of Au atoms [18].

The structure of liquid Au-Si alloys has been determined with X-ray diffraction measurements as a function of temperature [24] showing that it conforms to the model of the dense random packing of hard-sphere with Si atoms coordinating on average 10 Au atoms. Progressive slight densification was found as the temperature decreased down to the eutectic point for the composition $\text{Au}_{81}\text{Si}_{19}$. Simulation by ab-initio molecular dynamics showed strong intermixing of the two elements [25]. Should the coordination shell of Si be similarly filled at random by the metal atoms of the present alloy, half of them would be less noble than Au and, therefore, liable to dissolve together with the central Si atom. A subsequent movement at short range of Au atoms, some of which are already nearest neighbours, would enable clustering at multiple locations where fine crystals would form. At variance, in crystalline alloys the Au atoms cluster epitaxially on the fcc substrate.

After de-alloying for longer time (60 s) more atoms are dissolved and the height of the protuberances increases to 85-90 nm while their shape and size is modified. They appear made of bumps, some joined to each other but no one of them exceeding 100 nm in size, i. e. they are definitely smaller than the protuberances found earlier. The porosity around them clearly has increased in volume (Fig. 2 c and d) showing that there is a preference for atoms removal around the base of these features (Fig. 2 e and f). This seems to represent a similarity with the de-alloying of crystalline alloys where under-cutting of passivated mounds was suggested by Erlebacher et al. [10-12] at the beginning of formation of ligaments rich in Au atoms.

At the de-alloying time of 3 minutes, the surface is covered by gold particles around 100 nm in diameter, some of which appearing knobbly due to coarsening by growth and impingement on each other (Fig. 4a). After de-alloying for 5 minutes, the increase in size and agglomeration of surface features clearly continues (Fig. 4b) whereas after 10 minutes, the gold hills transformed into interconnected ligaments with porosity in between (Fig. 4c). The height of these ligaments exceeds 300 nm. There is clear evidence of coarsening by diffusion.

A slice of a sample de-alloyed for 15 min was cut from the ribbon by FIB and analyzed by STEM. Images show the network of ligaments expanding from the external surface into the bulk for about 500 nm (Fig. 5). Their size is uniform and of the same order as those shown in Fig. 4c, indicating that a steady state of coarsening has been reached. In between the ligaments and the pristine amorphous phase, an intermediate wavy layer around 50 nm thick is well distinguishable connecting the amorphous matrix to the ligaments (Fig. 5a,b). It is composed of filaments and channels. Observing these zones by HRTEM, a mixture of the amorphous phase with randomly oriented Au-nanocrystals, as well as a network of Au filaments of the order of 10 nm in size is found (Fig. 5c-d), i.e. the same microstructure as that of the sample mechanically thinned and de-alloyed for 30 s which was described above. Apparently this intermediate zone between the amorphous bulk phase and the polycrystalline ligaments demonstrates how the undercutting occurs and how the porosity evolves via percolation of the electrolyte in the newly formed channels.

Comparing this sample with another one that was de-alloyed for 60 minutes (Fig. 5c), the interface between the porous network and the amorphous alloy appears unchanged: about 50 nm thick with a similar de-alloying front. This is evidence that the same mechanism is operative also for later stages of the process.

The coarsening of ligaments brings about a typical microstructure as shown in Figs. 4 and in the TEM images of Fig. 6, where the crystals composing the ligaments display grooves on the external surface. Internally, they contain stacking faults or twin boundaries. The latter feature is indicative of a microstructure resulting from grain impingement. Actually, in a different context of encounters of nanoparticles floating in a liquid medium which gave rise to microstructures analogous to the present ones, the attachment between some of them occurred at favourable orientation with faults accounting for the mismatch in lattice stacking [30]. Models of coarsening after de-alloying crystalline alloys have appeared in the literature, suggesting ligament pinch-off due to Rayleigh instability which might

determine the topology of the ligament network [12]. At variance, a mechanically driven pinch-off and collapse of neighbouring ligaments onto each other has been proposed taking into account the local stresses due to atoms removal [14]. Our microscopy observations of de-alloyed amorphous alloy did not provide evidences in this context, but revealed the occurrence of an intermediate layer between amorphous matrix and grown ligaments in which the processes of germination and impingement take place. The fully de-alloyed ribbon was found to have undergone contraction of up to 30% in the direction of its thickness, whereas the width did not change appreciably. This is not surprising, since the ribbon is a few tens of microns thick, therefore the lateral contraction is negligible in comparison to its width. The amorphous backbone of the structure is present until the end of the process and must impose a shear stress on the intermediate layer. Since there is no direct evidence of ligaments breaking, it is concluded that the stress is distributed throughout the intermediate layer and the loss of volume results in the growth direction. This is a feature specific of amorphous alloys, which was never reported for the de-alloying of crystalline ones. A general finding related to this discussion is that the de-alloyed glassy ribbon is easily separated into two layers by a fracture surface occurring in its middle and corresponding to the last portion being etched [20]. (suppl. info text). The occurrence of shrinkage on de-alloying has been shown earlier in both crystalline binary alloys [27] and amorphous thin films [28]. Our findings show the relevance of the interlayer which progressively moves during the process in accommodating the intervening stresses in the case of amorphous ribbons. The size of ligaments depends primarily on the temperature at which the de-alloying is performed and on the type of electrolyte [18, 19].

The permanence of surface grooves even after prolonged etching is also a specific feature found in de-alloying of amorphous metals. This appears due to extensive surface diffusion during coarsening. The formation of grooves at triple points between a grain boundary and external grain surfaces was classically described as a surface diffusion phenomenon driven by the decrease in free energy caused by the movement of atoms away from the grain boundary [29]. The grooves are formed to establish a thermodynamic local equilibrium between the boundary and the intersected external surface. Since it is known that some less noble atoms remain trapped in the ligaments after de-alloying [32], it is deduced that these could be segregated to defects in case the partitioning is thermodynamically favoured. This can help in enhancing the chemical activity of the porous material which was shown to be active in catalysing the oxidation of methanol [17,20] and in enhancing the Raman response of adsorbed molecules [31].

Conclusions

In this work, the de-alloying mechanism during electrochemical etching an amorphous Au-based alloy has been disclosed for the first time by means of a set of microscopy observations: from the very early moments of etching up to the extensive development of a porous network.

A native layer of Si oxide was found on the surface of the alloy chosen for the experiments, $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$. The electrolyte penetrates through the cracks of the layer in a few seconds, forming channels and leaving protuberances of size of the order of

a few hundred nanometers. These are then excavated laterally and in depth to give isolated fine crystals at first and ligaments by impingement of the growing crystals.

The key feature shown in the early stages and in the subsequent movement of the interface between the porous layer and the matrix, is the occurrence of an interlayer about 50 nm in thickness formed by filaments, which are around 10 nm wide and voids, as well as residues of the amorphous phase embedded with Au nanocrystals.

Ligaments emerge from the interlayer after appropriate de-alloying time. They coarsen in a few minutes to a size dependent on the temperature at which the process is performed and do not change appreciably during the progress of de-alloying. The ligaments are made of adjoining fine crystals containing planar lattice defect. It is deduced that the nanocrystals formed at the interface with the amorphous phase grow by addition of Au atoms and impinge on each other, giving rise to a three dimensional scaffold. During these steps pores develop in between. In spite of the occurrence of these voids, a substantial portion (up to 30%) of the original volume of the material is lost. It is speculated that the interlayer sustains the stress due to shrinkage in the direction normal to that of growth.

The coarsened ligaments display grooves on the surface, apparently due to equilibrated grain boundaries.

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Figure captions

Fig. 1 : (a) AFM topography of the as-spun ribbon and (b) the XPS depth profile.

Fig. 2: HSEM (left) and AFM (right) images of $\text{Au}_{40}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ de-alloyed for 30 s (a, b) and 1 minute (c, d). Image of the cross-section of the sample de-alloyed for 1 minute (e) (HSEM) showing the "under-cutting" around the basis of the mounds.

Fig. 3: TEM image of a sample de-alloyed for 30 s. The inset reports the diffraction pattern containing both haloes and rings. (b) is an enlargement of (a) highlighting some fine crystals having different orientation of lattice fringes.

Fig. 4: AFM topography of the surface of ribbons de-alloyed for 3 minutes (a), 5 minutes (b) and 10 minutes (c). Arrows highlight impingement events between crystals.

Fig. 5: STEM images of the cross section of the sample de-alloyed for 15 minutes (a, b) and 60 minutes (c). high resolution TEM image showing the interlayer between the ligaments and the amorphous phase of the 15 minutes de-alloyed sample (d, e).

Fig. 6: TEM images of the sample de-alloyed for 30 minutes. (a) bright field image of the ligament network made of several crystalline grains separated by boundaries marked by arrows. The inset is the relative selected area electron diffraction in which dots due to Au crystals and amorphous halos appear. (b) high resolution TEM image showing the surface groove due to a grain boundary and the presence of stacking faults inside the crystal.











